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Produced water from CO_2-EOR in the Illinois Basin

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Abstract

Significant volumes of produced water might be available from future CO_2-enhanced oil recovery (CO_2-EOR) operations. Produced water can be considered as a potential resource if it can be treated and transported in a cost-effective manner. An estimation of potential quantity of produced water from EOR-CO_2 in the Illinois Basin (USA) and a detailed characterization of produced water samples are presented in this paper. A potential volume of 4.1 billion barrels of water from potential future CO_2-EOR operations in the twenty largest oilfields in Illinois Basin can be produced. Produced water samples, collected from four main Illinois oilfields, have high salinities and contain various major and trace species.

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Keywords: produced water; Illinois Basin; EOR; CO_2-EOR; oilfield; water quality

1. Introduction

Produced water is defined as the water from geological formations that is brought to the surface during production of fossil fuels. It is also referred to as production water, co-produced water, or formation water by different researchers. Produced water constitutes the single largest waste stream in the oil and gas industry [1]. The national average water-to-oil ratio estimated from the onshore production-weighted ratios of 14 states was 7.6 (barrel

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per barrel) [2]. The estimated yearly amount of produced water generated from onshore oil and gas activities in the United States from 1988 to 2007 varied between 14 and 21 billion barrels [2-5].

Depending on the produced water quality, current practice for produced water management includes reinjection into underground formations, surface discharge into receiving waters, and beneficial reuse. Water from surface mines and overflowing underground mines typically is discharged to surface streams, whereas reinjection is the most common approach for managing onshore oil and gas produced water. More than 98% of produced water from onshore wells was injected underground in 2007 [2]. Approximately 59% was injected into producing formations to maintain reservoir pressure and for enhanced oil recovery (EOR), while another 40% was injected into nonproducing formations for disposal [2].

The major constituents in oilfield-produced water include suspended solids, dispersed oil and grease, dissolved organic compounds, and various cations and anions. The physical and chemical properties of produced water vary widely depending on the geographic location of the field, the geological formation from which the water is pumped, and the composition of hydrocarbon products being produced. Considering the finite availability of freshwater resources and increasing demand for water in thermoelectric, agricultural, domestic, and industrial sectors, in addition to possible water shortages due to climate change, new restrictions on water use, even in non-arid areas, seem likely to be enacted. Non-traditional sources of water such as produced water may potentially become significant supplements to current freshwater sources for thermoelectric, industrial, and agricultural applications. Techno-economic feasibility of treatment and reuse of produced water depends on several factors including quantity of produced water resources, water quality, and transportation cost. The focus of this paper is on the estimation of the potential quantity of produced water from potential future EOR-CO_2 operations in the Illinois Basin and characterization of produced water quality.

2. Produced water quantity

A large volume of water can be produced during the EOR operations. EOR water flooding and oil production data from the Illinois State Geological Survey (ISGS) databases for years 2001-2006 was analyzed to estimate the average ratio of produced water to oil in Illinois. More details about data collection and analysis can be found in a recent report [6]. The average oil production from water flooding EOR is about 3.3 million barrels per year, which is about 30% of the total Illinois oil production. The total average yearly production of produced water from EOR water flooding activities is about 138 million barrels. Almost all of the produced water (>99%) from water flooding projects is re-injected into oilfields to continue oil production. The average water-to-oil ratio for all EOR water flooding activities for the six studied years was about 41.2.

There are more than 1,000 oilfields in the Illinois Basin that are potentially available for CO_2-EOR application. The potential amount of produced water from each oilfield depends on a variety of factors including geological characterization of the oilfields and specifications of the EOR technology. Total original oil in place (OOIP) of the Illinois Basin is estimated as 14.1 billion barrels and approximately 10% of this amount can be potentially recoverable by CO_2-EOR [7].

The twenty largest oilfields that initially contained 8.2 billion barrels, or ~58% of the total OOIP, were selected for this study (Figure 1). Detailed information about these oilfields including reservoir ranking, location, area of coverage, number of formations, estimated OOIP, estimated CO_2-EOR, estimated OOIP from the most important formations, depth of the formations, and estimated produced water from each oilfield and its most important formations is provided elsewhere [6].

The total potential produced water quantity was calculated by estimating the maximum volume of CO_2 that may displace water during oil production. After primary and secondary oil recovery, approximately 40% of OOIP is removed, and water from the producing formation fills regions previously occupied by oil. During CO_2-EOR, an additional ~10% of OOIP is recovered, and the entire region once occupied by oil is filled with CO_2. The estimate of water produced during CO_2-EOR is the total volume of oil removed from the reservoir. The OOIP of an oilfield (or formation) is multiplied by 0.5 to determine the volume of produced water. Based on these results a potential maximum amount of 4.1 billion barrels of water may be produced from the twenty largest oilfields in Illinois Basin during CO_2-EOR oil recovery.

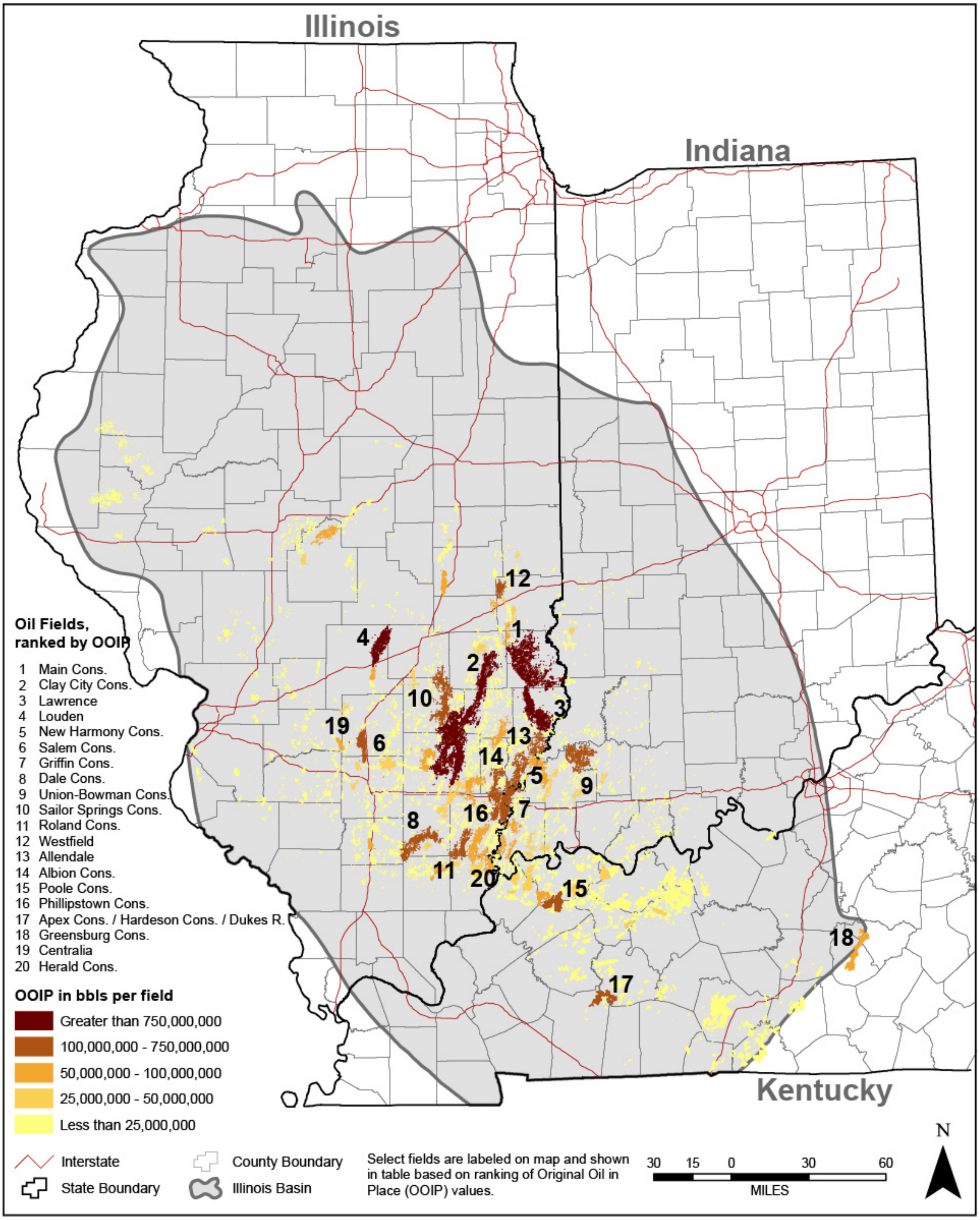

Figure 1: Geographic distribution and estimated amount of original oil in place (OOIP) of oilfields in the Illinois Basin (Twenty largest oilfields are ranked and shown. Information derived from Ref. [8]).

3. Produced water quality

3.1. Previous studies of produced water quality

The United States Geological Survey (USGS) and ISGS databases or reports were searched to obtain water quality data from the selected twenty largest potential CO_2-EOR oilfields in the Illinois Basin. The USGS database [9] contains sample data from various geologic formations. The Illinois data are from a 1952 ISGS study [10]. Additional data for the Aux Vases and Cypress Formations is available from a 1995 ISGS study [11]. Data from these fields was compiled, and the statistics obtained from the data are presented in Table 1. Produced water from these oilfields tends to be highly saline. The total dissolved solids (TDS) values for produced water ranged from 6,000 to 210,000 mg/L, with a large fraction of the TDS comprised of sodium and chloride ions. Most of the produced water samples with smaller TDS concentrations were collected from Pennsylvanian formations that are shallow compared to other formations. The produced water from the Roland Consolidated oilfield within the Waltersburg Formation had one of the lowest TDS values. The Sailor Springs field has TDS concentration in the range of 17,000 mg/L in the Tar Springs formation. The Clay City Consolidated oilfield has some of the highest (>150,000 mg/L) observed concentrations of TDS, in samples collected from the Ohara and McClosky Formations.

Statistical data for the concentrations of additional species reported by Demir [11] are shown in Table 2. Water quality data were averaged over the fields that are among the selected twenty fields in the Illinois Basin for two oil-producing formations (Aux Vases and Cypress). Concentrations of TDS and of various other ions are similar to values reported in the USGS database. Valuable elements such as lithium and iodine generally have small concentrations (less than 10 mg/L).

Table 1: Compiled data from USGS and ISGS (1995) reports for the twenty largest oilfields in the Illinois Basin. All units, except pH, are in mg/L.

	pH	**TDS**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**Cl^-**	**SO_4^{2-}**
Mean	6.6	110,000	37,000	4,300	1,300	220	68,000	810
SD	0.6	34,000	11,000	2,600	490	230	21,000	890

Table 2: Statistical summary of 1995 ISGS data from produced water sampled from the Aux Vases and Cypress Formations in the Clay City Consolidated, Lawrence, New Harmony, Dale, Sailor Springs, and Roland oilfields within Illinois. All units, except pH, are in mg/L.

	pH	**TDS**	**Cl^-**	**Br^-**	**I^-**	**SO_4^{2-}**	**HCO_3^-**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**	**K^+**	**Sr^{2+}**	**NH_4**	**Ba^{2+}**	**Li^+**	**Fe**	**Mn**	**B**	**Si**
Aux Vases																			
Mean	6.7	125,634	73,996	154	9	612	122	44,193	4,721	1,488	222	265	30	3	8	8	1	4	5
SD	0.6	24,472	14,608	43	3	572	53	8,554	1,348	438	66	206	8	5	3	14	1	1	2
Cypress																			
Mean	6.4	106,041	62,333	127	4	551	202	38,347	3,079	1,075	128	132	22	18	5	7	2	3	6
SD	0.6	25,218	14,822	35	2	471	170	8,943	1,427	296	42	94	9	52	4	6	2	0	4

The quality of produced water from oilfields in the Illinois Basin has significant variability. Figure 2 shows the cumulative distribution of histograms of TDS and chloride concentrations for produced water from the top twenty oilfields, using data from the USGS database and the 1995 ISGS publication. The cumulative distribution is calculated by dividing the number of samples with concentrations less than a given value by the total number of samples. Cumulative distributions are calculated separately for the ISGS data (29 samples) and the USGS data (279 samples). Most produced water samples have TDS concentrations in the range of 100,000 to 150,000 mg/L, but a few samples (4%) have concentrations less than 30,000 mg/L. The chloride concentration distribution shown in

Figure 2b and the high chloride and sodium concentrations listed in Tables 1 and 2 show that most of the TDS is composed of sodium chloride.

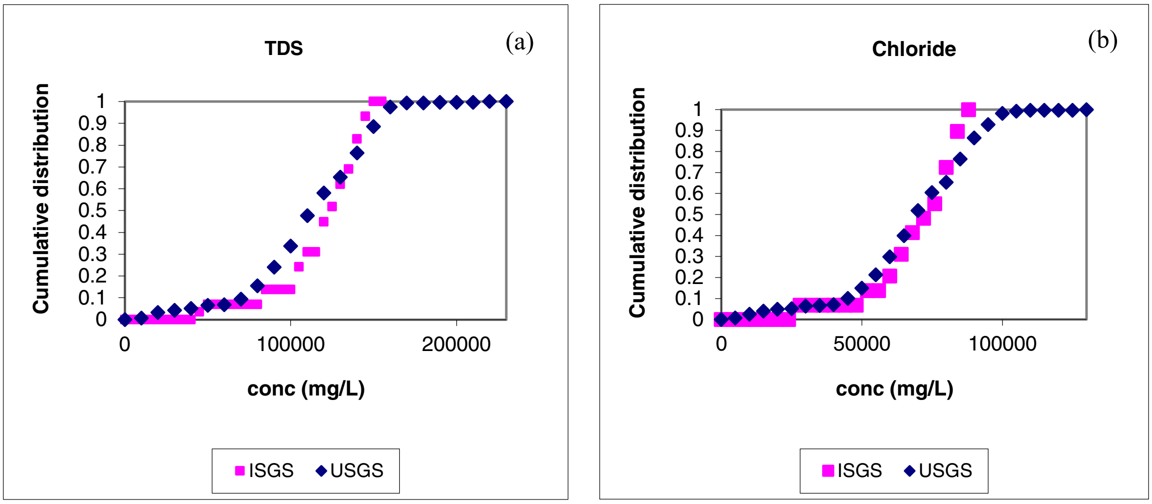

Figure 2: Concentration distributions for (a) TDS and (b) chloride for the USGS and 1995 ISGS data sets. There are 279 and 29 data points for the USGS and ISGS (1995) reports, respectively.

3.2. Produced water sampling and characterization

Water samples were collected from four oilfields (Main Consolidated, Louden, Dale, and Sugar Creek) that are among the largest fields in the Illinois Basin. Water from the sampling sites was collected primarily from composite sources rather than from individual wells. Water collection procedures followed the guidelines established by the USGS water sampling field manual [12]. More details about water sampling and preparation are provided in a previous report [6].

Sample preparation and analysis procedures are schematically shown in Figure 3. Produced water samples were analyzed for pH, conductivity, turbidity, TDS, total suspended solids (TSS), alkalinity, total petroleum hydrocarbons (TPH), selected cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, and Sr^{2+}) and anions (Cl^-, Br^-, and HCO_3^-), ammonia, and dissolved organic carbon (DOC) concentrations, using standard methods [6]. Quality assurance for analyses was provided by analyzing selected duplicate samples, blank samples, and spiked samples.

Water quality parameters, including pH, turbidity, conductivity, TDS, TSS, alkalinity, DOC, and ammonia content, are presented in Table 3. Included in the table are the average values and standard deviations of these parameters.

For the samples analyzed for this study, the pH values are between 6.4 and 7.4 and are consistent with those of the twenty largest oilfields in the Illinois Basin with a mean of 6.6±0.6 (Table 1). The turbidity of unfiltered samples ranged from 13 to 420 Nephelometric Turbidity Unit (NTU) (Table 3). The turbidity of samples from the same sampling source also varied widely among different sites, suggesting that turbidity may not be determined by the geological formation, but more influenced by the site operation of wells. After filtration, all samples had turbidities of less than 1 NTU.

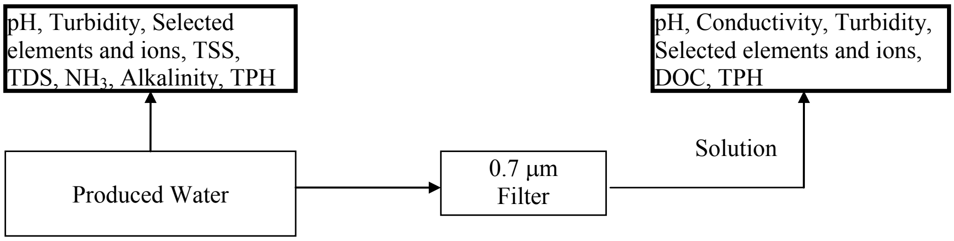

Figure 3: A schematic diagram of produced water sample preparation and analysis.

TDS ranged from 19,010 to 126,949 mg/L (Table 3). For comparison, the TDS value for the national drinking water standards recommendation for potable water is 500 mg/L [13]; the TDS of seawater is about 35,000 mg/L [14]; and the TDS of produced water in the Western United States ranges from 1,000 to 400,000 mg/L [15]. A significant correlation between TDS and conductivity was observed for oilfield brines: TDS (g/L) = Conductivity (mS/cm) × 0.80 ($R^2 = 0.97$). And the coefficient of 0.80 is within the reported range of 0.54 – 0.96 for natural waters [16].

TSS ranged from 8 to 136 mg/L, alkalinity from 90 to 1,148 mg/L, and DOC from 6 to 508 mg/L (Table 3). The concentration of ammonia (primarily in the form of NH_4^+ within the sample pH ranges) ranged from 0 to 36 mg N/L.

The TPH contents of selected samples before and after filtration are presented in Figure 4. The TPH content of samples from oilfields (ranging from 26 to 107 mg/L) was reduced by 71 to 95% after passing through the 0.7 µm filter, which indicates that the majority of TPH in water samples was associated with suspended small droplets, colloids, and particles. For comparison, the oil and grease contents of produced water in the Western United States range from 40 to 2,000 mg/L [15].

Concentrations of selected cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, and Sr^{2+}) and anions (Cl^-, Br^-, and HCO_3^-) in sampled produced water are presented in Table 4. Na^+ is the dominant cation in all samples, followed by Ca^{2+}, while chloride was the most abundant anion in all samples. The mean Na^+, Ca^{2+}, and Cl^- concentrations in samples from the four oilfields (Table 4) were lower than the mean values for the twenty largest oilfields reported in the previous studies (Tables 1 and 2). Linear correlations were observed between TDS and Na^+ and Cl^- concentrations ($R^2 = 0.92$, and 0.94 for Na^+ and Cl^-). Concentrations of HCO_3^- were calculated from alkalinity and pH values. The mean HCO_3^- concentration in oilfield samples was 620±505 mg/L.

Table 3: Water quality parameters of selected filtered (F) and unfiltered (U) produced water samples.

Source	Site	pH	Turbidity (NTU)		Conductivity (mS/cm)	TDS (mg/L)	TSS (mg/L)	Alkalinity (mg/L as $CaCO_3$)	DOC (mg/L)	Ammonia (mg N/L)
		U	U	F	F	F	U	U	F	U
Main Consolidated	1	7.0	420	0.2	32	19,010	101	1,148	508	4
	2	7.2	96	0.9	24	22,043	136	595	14	0
	3	7.4	97	0.6	33	20,807	74	1,109	11	0
Louden	1	7.4	33	0.1	120	101,734	9	285	9	25
	2	6.7	13	0.2	140	102,650	104	163	6	25
	3	6.9	49	0.4	100	90,557	48	238	7	24
Dale	1	6.7	36	0.1	160	126,949	8	90	20	32
	2	7.1	74	0.2	89	78,200	75	178	7	36
Sugar Creek	1	6.4	168	0.2	39	25,317	17	776	15	5
Mean of Oilfields		7.0 ±0.3	110 ±125	0.3 ±0.3	82 ±52	65,252 ±43,185	63 ±46	509 ±415	66 ±166	17 ±14

Concentrations of trace elements in samples are shown in Table 4. Boron (B) and Si were detected in all samples. The mean concentration of B and Si were 3±2 and 6±1 mg/L, respectively. Boron concentrations in samples from Dale oilfield (5 and 6 mg/L) were comparable to that of seawater (4.5 mg/L) [17]. The average concentrations of B and Si for 41 water samples from selected oilfields in the Aux Vases Formation in the Illinois Basin were 3.90±1.39 and 4.50±1.60 mg/L, respectively; and the average concentrations of B and Si for 36 water samples from selected oilfields in the Cypress Formation in the Illinois Basin were 2.58±0.57 and 5.00±2.80 mg/L, respectively [18]; not significantly different from our results. The average concentration of Li in oilfield water samples was 5±3 mg/L, similar to that in 41 water samples from selected oilfields in the Aux Vases Formation (8.22±3.04 mg/L), and in 36 water samples from selected oilfields in the Cypress Formation (4.96±0.36 mg/L) [18], but these values are more than an order of magnitude greater than normal concentration of Li in seawater (0.17 mg/L) [19]. Concentrations of Cu, Mn, Ni, and Fe (not shown in Table 4) in most samples were less than 1 mg/L.

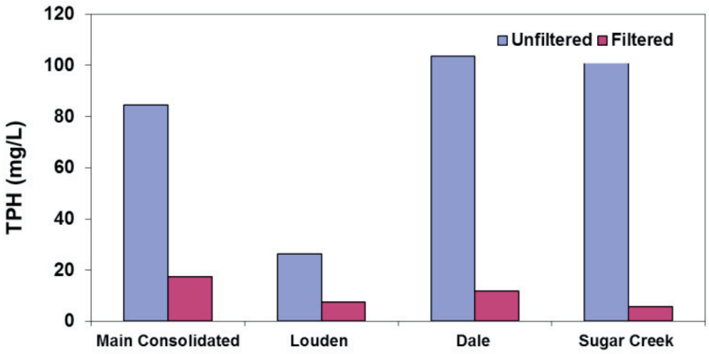

Figure 4: Total petroleum hydrocarbons (TPH) contents in selected samples before and after filtration.

Table 4: Concentrations of major and trace species in produced water samples. All units are in mg/L.

Source	Site	Na^+	K^+	Ca^{2+}	Mg^{2+}	Ba^{2+}	Sr^{2+}	Cl^-	Br^-	HCO_3^-	B	Si	Li
Main Consolidated	1	7,110	32	200	184	34	13	10,421	28	1,400	1	5	BD
	2	7,910	26	374	167	138	26	12,410	27	724	1	6	BD
	3	7,302	26	299	178	99	21	11,635	33	1,350	1	8	BD
Louden	1	33,568	101	2,603	969	610	219	60,341	95	346	3	5	3
	2	32,547	100	2,615	999	314	185	58,277	90	199	3	4	3
	3	31,877	100	2,509	984	430	195	58,118	90	290	2	5	3
Dale	1	38,958	244	4,892	1,603	2	303	74,884	124	110	5	6	9
	2	37,356	239	3,988	1,325	1	194	65,814	110	216	6	6	8
Sugar Creek	1	7,961	19	603	219	3	331	14,012	71	946	2	6	BD
Mean of Oilfields		22,732 ±14,554	98 ±88	2,009 ±1,733	736 ±558	181 ±221	165 ±120	40,657 ±27,549	74 ±37	620 ±505	3 ±2	6 ±1	5 ±3

BD: below detection limit.

4. Conclusions

Produced water from CO_2-EOR can be considered as a potential resource for beneficial use if it can be treated and transported in a cost-effective manner. Techno-economic feasibility of produced water reuse depends on several factors including quantity and quality of produced water resources. The potential amount of produced water from future CO_2-EOR operations in the twenty largest oilfields in the Illinois Basin is estimated as 4.1 billion barrels. Produced water sources are located throughout the southern half of the Illinois Basin. Significant uncertainties make precise estimation of produced water quantity difficult. Development of CO_2-EOR projects depend on the cost and availability of CO_2, oil price, and future regulations for CO_2 emission and brine disposal. Water quality of each of the sources of produced water varies significantly. TDS concentrations of water samples collected in this study ranged between 19,000 and 127,000 mg/L. The dominant components in all produced waters were sodium and chloride but water samples also contained other major and trace species.

Acknowledgements

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